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PAUL BELLVILLE TAYLOR

A THESIS

IN PHYSICS

PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL IN
PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
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Reprint from

THE JOURNAL OF PHYSICAL CHEMISTRY

Vol. XXXI, No. 10.

PHILADELPHIA

1927

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ELECTROMOTIVE FORCE OF THE CELL WITH TRANSFERENCE AND THEORY OF INTERDIFFUSION OF ELECTROLYTES

BY PAUL B. TAYLOR

A recent paper by Harned[1] on the thermodynamic behavior of individual ions is representative of the persistent attempts which have been made to establish a basis for the determination of the free energies of ions by means of the cell with transference, i.e., a cell containing a junction of two (different) electrolytes. The present analytical study leads to the conclusion that the EMF of the cell with transference is a function of free energies which are molecular only, that it can not possibly be manipulated to yield ionic free energies, and that the ionic free energy has not been thermodynamically defined. It is to be thought of rather as a purely mathematical device, which may indeed be employed safely with considerable freedom.

Electromotive Force of Cell with Transference as an Integral

In order to avoid a burdensome accretion of constant multipliers we shall measure concentration in reciprocal Faradays, i.e., the quantity of ionic species associated with one coulomb of electricity, per unit volume. Explicit reference to valence is thus generally avoided. We shall measure all free energies directly in joules per coulomb, i.e., in volts, and choose a temperature such that RT = 1. In the final formulae the factor RT/F may be restored and molalities divided by valence may replace concentrations; the formulae then become valid for customary units.

Consider the cell with transference:

$$(1) \mid m_1, m_2, --- m_i, --- \mid m'_1, m'_2, --- m'_i --- \mid (1)$$

The m's denote the concentrations of the various component ionic species in the left hand half of the cell, m''s those in the right. Odd subscripts denote cations, even anions, i denotes the typical ion of either sign. For definiteness the ion to which the electrodes are reversible, (1), has been chosen a cation.

Initially let the cell be one in which no transfer of solvent occurs either thru hydration or thru crystallization. Further let the concentrations in the two half cells differ by infinitesimals. Following the sign convention of Lewis and Randall the EMF of the cell, dE_{1t}, is given by

$$dE_{1t} = dF_1 - t_1dF_1 + t_2dF_2 - t_3dF_3 \pm ---, \qquad (1)$$

where dF_i stands for the increase in free energy of ion i on passing from left to right, and t_i stands for its transference number, the fraction of current carried by ion i when the circuit is closed thru infinite resistance.

Now from a cell without transference of the type,

$$(1) \mid m_1, m_2, --- m_i --- \mid (2) \mid m'_1, m'_2, --- m'_i --- \mid (1),$$

[1] Harned: J. Phys. Chem., 30, 433 (1926).

whose observed EMF is dE_{12}, we have

$$\begin{aligned} dE_{12} &= dF_1 + dF_2 \\ dF_2 &= dE_{12} - dF_1. \end{aligned} \qquad (2)$$

Similar cells may be set up for each of the other anions with similar equations.

Likewise the cell

$$(1) \mid m_1, m_2, m_3 \text{ ---} \mid (3) \mid m'_1, m'_2, m'_3, \text{ ---} \mid (1),$$

whose EMF is dE_{13}, gives

$$\begin{aligned} dE_{13} &= dF_1 - dF_3 \\ dF_3 &= dF_1 - dE_{13}; \end{aligned} \qquad (3)$$

and similar equations hold for each of the other cations.

These values for dF_2, dF_3, --- being substituted, (1) becomes

$$dE_{1t} = dF_1 - t_1 dF_1 + t_2 (dE_{12} - dF_1) - t_3 (dF_1 - dE_{13}) \pm \text{---}$$
$$= dF_1 - (t_1 + t_2 + t_3 + \text{---}) dF_1 + t_2 dE_{12} + t_3 dE_{13} + \text{---}.$$

But

$$t_1 + t_2 + t_3 + \text{---} = 1.$$

Hence

$$dE_{1t} = t_2 dE_{12} + t_3 dE_{13} + \text{---}, \qquad (4)$$

and for a cell in which the concentrations vary continuously from one side to the other thru a finite range

$$E_{1t} = \int t_2 dE_{12} + \int t_3 dE_{13} + \text{---}. \qquad (5)$$

For the cell with electrodes reversible to an anion the same formula is arrived at, cation and anion subscripts being permuted. Hence, if 1 be taken to denote the ion of the electrode, odd subscripts to denote ions of like sign, even subscripts ions of contrary sign, (5) *becomes the general expression for the EMF of the cell with transference in terms of the corresponding cells without transference.*

When the number of ionic species is but two, the right hand member of (5) reduces to a single term, and will be recognized as a formula which has long been known.[1,2]

All terms in the ionic free energies have now been eliminated and E_{1t} expressed entirely in terms of transference numbers and EMF's of cells without transference, which latter may all be considered *molecular* free energies. If it be conceded that the transference numbers are not functions of the ionic free energies nor are the correction terms for transference of solvent (we shall presently prove both) our principal point is established, namely, that the EMF of a cell with transference is a function of molecular free energies only.

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[1] Helmholtz: Wied. Ann. **3**, 201 (1878); Ber., **7**, 27 (1882); Collected Papers **1**, 840; **2**, 979.

[2] MacInnes: J. Am. Chem. Soc., **37**, 230 (1915).

Correction for Transference of Solvent

The expression for cell EMF is now to be corrected for the effect of transfer of solvent from one side of the cell to the other due to hydration of the ions and to solvent of crystallization. Let equations (1), (2), (3) be now the respective definitions of the quantities E_{1t}, E_{12}, E_{13}, − − −, and let the actual EMF's of the corresponding cells be denoted by italics, E_{1t}, E_{12}, E_{13}, − − −. Let s_i represent the quantity of solvent which due to crystallization with ion i is effectively transferred by ion i from left to right per unit of positive electricity flowing thru a cell from left to right. Let s_o represent that transferred due to hydration. Let dF_s represent the differential of increase in free energy of the solvent on passing from left to right.

The EMF of the cell with transference is now given by

$$dE_{1t} = dF_1 - t_1 dF_1 + t_2 dF_2 \pm - - - - (s_o + s_1) dF_s.$$

The EMF's of the cells without transference become

$$dE_{12} = dE_{12} - (s_2 + s_1)\, dF_s$$
$$dE_{13} = dE_{13} - (s_3 + s_1)\, dF_s.$$

Integrating, the EMF of the cell with transference becomes

$$E_{1t} = E_{1t} - \int (s_o + s_1)\, dF_s, \qquad (6)$$

or

$$E_1t = \int t_2 dE_{12} + \int t_3\, dE_{13} + - - - + \int (-s_o - t_1 s_1 + t_2 s_2 + t_3 s_3 + - -) dF_s.$$

It is possible that other molecular species might be transferred in the same way as the solvent. In such case other terms similar to those in dF_s would need be added. With the inclusion of such terms equation (6) is exact. Obviously ionic free energies do not occur in these correction terms.

The transference numbers now remain to be examined. It is at least conceivable that dE_{1t} might be an exact differential and that E_{1t} might depend only on the initial and final concentrations, but theory[1] and experiment both show that it depends also on the manner in which the junction of the electrolytes is established. (One exception is the case of the cell with a single binary electrolyte; this case is too well understood to warrant any special attention.) In order to integrate (5) it is then impossible to avoid the necessity for expressing the molecular free energies, ionic mobilities, and concentrations thruout the cell in terms of a single variable. The distribution of these quantities depends on the manner of forming the junction, which may be in a variety of ways. One way is to connect the electrodes by a series of pools, each of which differs in composition from its neighbors by arbitrary small amounts. The distribution is then known and there is no theoretical impediment to the evaluation of E_{1t}. Plainly the transference numbers would not be functions of free energies. In particular the distribution may by this means be made that of Henderson (vid. Eq. (37)).

[1] Beatty: J. Am. Chem. Soc., **46**, 2211 (1924).

In all other cases the distribution of concentrations will depend not only on the manner of establishing and maintaining the junction but also on the specific ionic properties of diffusion. This latter condition we shall now express by exhibiting the concentrations as solutions of a set of differential equations.

Interdiffusion of Electrolytes

Consider two electrolytes in the process of interdiffusion in gravitational equilibrium. This is accomplished if the denser liquid is the lower, and forces of weight may then be neglected. It will be convenient to think of the cell as of unit cross section. Let us take the X axis vertical, origin arbitrary, and denote by m_i, the concentration of ionic species i at coordinate x and time t, by q_i its flux (quantity crossing unit section of the plane $x = c$ per unit time).

We define the mobility, u_i, by

$$u_i = q_i/(m_i \times (\text{force field})).$$

It must be sharply distinguished from the equivalent ionic conductivity, λ_i, which is defined by

$$\lambda_i = q_i/(m_i \times (\text{electrostatic field})).$$

If some of the ions are shielded from the full force of the electrostatic field the effective force is less than the electrostatic field, and λ is less than u. Since Ohm's law holds for electrolytes, λ is independent of the strength of the electrical field, and hence u is independent of the applied force (the more so that the forces in the present case are very small). λ and u may vary with the concentration.

We define the quantity, α_i, by

$$\alpha_i = \frac{\lambda_i}{u_i}.$$

It is called the degree of dissociation (not to be confused with the thermodynamic degree of dissociation or activity coefficient, γ). It is a measure of the fraction of (concentration $\times$ electrostatic field) which is effective in the flux. The effect may be due to incomplete dissociation of the ions but the actual cause is not implied.

Write the negative gradient of the ionic free energy

$$P_i = \frac{-dF_i}{dx}.$$

If now each ion diffused independently we should have the fluxes given by

$$q_i = u_i m_i P_i,$$

and the concentrations would be found as solutions of the equations of continuity

$$-\left(\frac{dm_i}{dt}\right)_x = \left(\frac{dq_i}{dx}\right)_t.$$

But since the total concentrations of cation and anion must remain everywhere equal there must be other forces besides the P's, say Q's. These Q's

are a set of mutual forces between the ions by which this equality is preserved. (Strictly the P's and Q's are forces per coulomb.) The fluxes are now

$$q_i = u_i m_i (P_i + Q_i ,) \tag{7}$$

and the equations of continuity

$$-\frac{dm_i}{dt} = \frac{d}{dx}[u_i m_i (P_i + Q_i)] . \tag{8}$$

Since the energy of the system is a function solely of the free energies, the Q's can do no work and hence must form a set of internal constraints in equilibrium. They are determined by the following conditions (9):

The flux of cation equals the flux of anion, or (distinguishing anions by subscript j)

$$i\sum u_i m_i (P_i + Q_i) = j\sum u_j m_j (P_j + Q_j) .$$

The Q's form a system of forces in equilibrium, or

$$i\sum m_i Q_i + j\sum m_j Q_j = o .$$

The rate of working of these forces is zero, or

$$i\sum u_i m_i (P_i + Q_i) Q_i + j\sum u_j m_j (P_j + Q_j) Q_j = o .$$

Also the concentration of cation equals that of anion, or

$$i\sum m_i = j\sum m_j .$$

We shall now divide the flux of each ionic species into two parts which we shall designate as the ionized and the unionized. We shall define the ionized portion of the flux as that portion which is affected to the full extent by a uniform impressed electric field. Any portion which is so affected is necessarily also affected to the full extent by a microscopic interionic field. Denoting it by subscript α we have for each ionic species

$$q_{i\alpha} = u_i m_{i\alpha} (P_i + Q_{i\alpha}) . \tag{10}$$

From the definition of α_i we have

$$m_{i\alpha} = \alpha_i m_i ,$$

and also now we have

$$-Q_{1\alpha} = -Q_{3\alpha} = --- = Q_{2\alpha} = Q_{4\alpha} = --- = Q_\alpha .$$

In exactly similar fashion we may now divide the unionized flux into a portion for which the Q's are equal and a remainder for which they are not. Denote the portion of the concentration so included by

$$m_{i\beta} = \beta_i m_i .$$

This subdivision may be repeated until the whole flux of all ions is partitioned into groups each with a common Q, or until completely associated molecules only remain, and within each molecule we must have the Q's equal.

From the solenoidal character of electrical induction it follows that equations (9) hold separately for each group and the fact that in each group the Q's are equal makes possible a solution.

The solution for the typical group is

$$Q_\alpha = \frac{u_1 m_{1\alpha} P_1 - u_2 m_{2\alpha} P_2 \pm - - -}{u_1 m_{1\alpha} + u_2 m_{2\alpha} + - - - -} . \tag{11}$$

Inserting the values of Q_α in (10) yields

$$q_{i\alpha} = u_i m_{i\alpha} \frac{u_1 m_{1\alpha} (P_i \mp P_1) + u_2 m_{2\alpha} (P_i \pm P_2) + - - -}{u_1 m_{1\alpha} + u_2 m_{2\alpha} + - - -} . \tag{12}$$

Here and elsewhere the upper sign is to be taken for i a cation, the lower i an anion.
But

$$P_i \mp P_1 = - \frac{dF_i}{dx} \pm \frac{dF_1}{dx} = - \frac{dE_{i1}}{dx}$$

$$P_i \pm P_2 = - \frac{dF_i}{dx} \mp \frac{dF_2}{dx} = - \frac{dE_{i2}}{dx} ,$$

and (12) becomes

$$- q_{i\alpha} = u_i m_{i\alpha} \frac{u_1 m_{1\alpha} dE_{i1} + u_2 m_{2\alpha} dE_{i2}}{(u_1 m_{1\alpha} + u_2 m_{2\alpha} + - -) \, dx} . \tag{13}$$

The equations of continuity becomes

$$\frac{dm_i}{dt} = - \frac{dq_{i\alpha}}{dx} - \frac{dq_{i\beta}}{dx} - - - -$$

$$= \frac{d}{dx} \left[u_i m_{i\alpha} \frac{u_1 m_{1\alpha} dE_{i1} + u_2 m_{2\alpha} dE_{i2} + - -}{(u_1 m_{1\alpha} + u_2 m_{2\alpha} + - - -) \, dx} + - - \right] . \tag{14}$$

Since the u's, E's, α's, β's $- - -$ are function only of (all) the m's, *the total of these equations for all species form the set of dynamical equations, the solutions of which together with the arbitrary boundary conditions in time and space completely determine the state of the system.*[1] In particular they determine the concentrations at every point.

Ionic Free Energies not unique

Since the ionic free energies, the F's have been eliminated from (14) they will be absent from any expression for the concentrations, the m's, which satisfies (14). It is permissible to say that any function from which the ionic free energies can be eliminated by substitution of molecular energies is a function of the latter and not of the former. We have already shown that ionic energies can enter the cell EMF only thru the transference numbers, and the transference numbers only thru the concentrations. Being absent from the concentrations they are then absent from both transference numbers and cell EMF. *The EMF of the cell with transference is thus a function of molecular free energies solely and is not a function of ionic free energies. It therefore can yield no information whatsoever concerning ionic energies.* In fact no thermo-

[1] We have restricted the system to one which varies in the X direction only. This restriction is removed by replacing d/dx by the Laplacian operator ∇.

dynamic information can be gained from a cell with transference which could not better be gained from a cell without transference. Conversely, within our present purview a knowledge of the ionic energies is never necessary for an account of the thermodynamics of electrolytes. Indeed, with the possible exceptions of single electrode potentials and rates of reaction there appears to be no occasion for the use of ionic free energies as experimental quantities but only as a mathematical device.

If any one ionic free energy in a solution be fixed, all the rest of the ionic free energies in that solution are determined thru the molecular energies. It now follows that for thermodynamic purposes we are at complete liberty to choose arbitrarily in each solution the free energy of any one ion, or more generally to set up for each solution any single arbitrary functional relation between the ionic energies (not a function of the molecular energies). In addition we may, of course, in any one solution choose arbitrarily every ionic energy. The ionic free energies thus determined have meaning only as they are referred to the arbitrary function but no thermodynamic inconsistencies will result from such procedure. This really puts into our hands a powerful tool for abridging computation. For instance we may take the free energy of one ionic species everywhere as zero and thus eliminate one term from a series; we may take the free energy of one cation equal to that one anion, or the total energy of cation equal to the total of anion.

An example of this use of partial energies is given in the paper cited of Harned's.[1] He there writes for the p.d. of the liquid junction (solvent transfer being neglected)

$$E_l = -i\sum \frac{RT}{v_i F} \int t_i d \ln a_i,$$

v_i being valence and a_i activity of ion i.

The value of the cell EMF in terms of E_l is

$$E_{lt} = ({}_2F_1 - {}_1F_1) + E_l,$$

where the F's are the free energies of the ion of the electrodes in the two half-cells. Harned evaluates E_{lt} from known data computing the two terms separately. To do this he postulates for one ion pair the relation

$$dF_K = dF_{Cl}.$$

The value of E_{lt} so computed is found to agree with the observed value; but this is not to be taken as a verification of the postulate, for he shows that another relation between dF_K and dF_{Cl} yields the same result, and we see from the foregoing that it would likewise be obtained on the basis of any relation whatsoever (subject to the sum of dF_K and dF_{Cl} being correct). The agreement is then to be taken as a verification of the formal correctness of his modification of the Henderson formula for the liquid junction p. d., E_l; it does not verify the numerical accuracy of this term in any absolute sense.

[1] J. Phys. Chem., 30, 433 (1926).

Another instance of the successful arbitrary employment of ionic free energies is in the so called law of additivity of ionic free energies. This law is usually stated on the assumption that the free energy of K and Cl are always equal, but clearly it is just as correct if based on equality for any other two ions. It is indeed a *molecular law* and not ionic at all. However, insofar as the law is a fact it is only to be explained on the basis of an *ionic theory*, and the use of ionic free energies for such purposes is natural and desirable. The law of additivity is only approximate, but some universal function must exist which *will* give the free energies of each molecular species in any electrolyte. This will be a function of various quantities, one or more for each ionic species present, which quantities will be capable of experimental determination. It may be found useful to construct some subordinate function of these quantities and call it the ionic free energy, but until the universal function is found there is no occasion for the subordinate one.

Concentration Distribution across a Junction

Equations (14) will now be used to find the distribution of concentrations in the junction as ordinarily formed and the cell EMF for that distribution.

The treatment thus far has been rigorous. Application of the theory is hampered, however, by our ignorance of the quantities u and α, not to speak of β, etc. The old theory of Kohlrausch considered that the mobility, u, was constant at all concentrations for each ion and that the degree of dissociation, α, varied with the equivalent conductance, λ. There is much excellent modern evidence for considering that α is constant (unity) and that u varies.[1,2] The direct determination of the u's should be possible from the coefficients of diffusion, but the author is not aware of any recent use of such data.

We shall now restrict our consideration to the case of the Q's being equal, i. e.,

$$-Q_1 = - - - = Q_2 = - - - - = Q$$

This means at any one place in the solution each ionic species is affected to the same extent by the surrounding inter-ionic field. All species will then be affected equally by an externally impressed field, whence

$$\alpha_1 = \alpha_2 = - - - - = \alpha .$$

This may be called the case of equal ionization; and these relations will be assumed for the remainder of this paper. They are probably correct for all concentrations of strong electrolytes (as Debye has shown). The treatment here permits α to be different from unity (incomplete ionization) and to vary with the concentration.

The common value of Q which satisfies equations (9) is now satisfied by

$$-Q_1 = - - - - = Q_2 = - - - - = Q$$

$$Q = \frac{u_1 m_1 dF_1 - u_2 m_2 dF_2 \pm - - -}{(u_1 m_1 + u_2 m_2 + - - -)dx} . \qquad (15)$$

[1] Debye: Physik. Z., **24**, 185 (1923) etc.

[2] Onsager: Physik. Z., **27**, 388 (1926).

Cf. (11).

$$-q_i = u_i m_i \frac{u_1 m_1 (dF_i) \mp dF_1) + u_2 m_2 (dF_i \pm dF_2) + - -}{(u_1 m_1 + u_2 m_2 + - - -) \, dx} . \quad (16)$$

Cf. (12).

The equations of continuity (8) become

$$\frac{dm_i}{dt} = \frac{d}{dx} u_i m_i \frac{u_1 m_1 (dF_i \mp dF_1) + u_2 m_2 (dF_i \pm dF_2) + - -}{(u_1 m_1 + u_2 m_2 + - - -) \, dx} . \quad (17)$$

Cf. (14).

These equations will now be integrated for the following conditions Consider that the two electrolytes of the half cell are initially brought together over the plane $x = 0$ at $t = 0$, that there are no other forces applied than the P's and Q's, and that the electrolytes extend away into a region that is not sensibly affected by the diffusion, i. e., to a physical infinity. It is not necessary that the initial physical distribution be exactly as described, for it is the property of diffusion that states initially different become in the course of time more and more alike.

Denote the concentration of ionic species i in the left hand half-cell (at $-\infty$) by M_i in the right hand (at $+\infty$) by M'_i. Write

$$\overline{M}_i = \tfrac{1}{2} (M_i + M'_i)$$

$$\triangle_i = \tfrac{1}{2} (M'_i - M_i) .$$

(7) may now be put in the form

$$q_i = - \int_{-\infty}^{x} \frac{dm_i}{dt} \, dx = u_i m_i (P_i \pm Q) . \quad (18)$$

It is now necessary to know the P's and u's as functions of the m's. The first approximation is

$$u_i = \text{a constant} ,$$

$$F_i = \frac{1}{v_i} \log m_i .$$

v_i is the valence (T has been chosen so that RT is unity). Hence

$$P_i = - \frac{dm_i}{v_i m_i dx} ,$$

$$Q = - \frac{\frac{u_1}{v_1} dm_1 - \frac{u_2}{v_2} dm_2 \pm - - -}{(u_1 m_1 + u_2 m_2 + - - - -) \, dx} . \quad (19)$$

The equation of continuity (17) becomes

$$- \frac{dm_i}{dt} = \frac{d}{dx} \left[- \frac{u_i}{v_i} \frac{dm_i}{dx} \pm u_i m_i \frac{\frac{u_1}{v_1} dm_1 - \frac{u_2}{v_2} dm_2 \pm - - -}{(u_1 m_1 + u_2 m_2 + - - -) dx} \right] . \quad (20)$$

In the special case that the u/v's are all equal to a common constant C^2, Q vanishes and (20) becomes

$$\frac{dm_i}{dt} = -\frac{d}{dx}\left(u_i m_i P_i\right) = C^2 \frac{d^2 m_i}{dx^2}.$$

The solution is well known[1]

$$m_i = \triangle_i \int^z \frac{2}{\sqrt{\pi}} e^{-(z/C)^2} \frac{dz}{C} + \overline{M}_i, \qquad (21)$$

where $z = \frac{x}{2\sqrt{t}}$.

The integral is the Gaussian probability function of zero order, Π_o, in terms of which

$$m_i = \triangle_i \Pi_o\left(\frac{z}{C}\right) + \overline{M}_i.$$

The solution will now be extended to the case that the u's are different. Since the u's are constant it follows from the principle of dynamical similitude that x and t can enter with the u's an expression for the m's only as functions of x^2/t. For the u's are of the dimensions t/x^2 and a change in the *units* of length and time cannot alter the m's. (the dimensions of the m's may be taken as the third fundamental unit.) Hence it must always be possible to write the m's as functions of z as defined above.

(21) yields (for the u's equal)

$$\frac{dm_i}{dt} = \triangle_i \frac{2}{\sqrt{\pi}} e^{-(z/C)^2} \frac{dz}{C\,dt}.$$

The solution for the u's not equal is gotten by considering that this may be altered at time t into any other permissible function whatsoever (consistent with the boundary conditions) by applying a correction factor (if $\triangle_i \neq o$). The Weierstrassian differential so obtained is

$$\frac{dm_i}{dt} = \triangle_i \left[\frac{2}{\sqrt{\pi}} A_i + 2B_i \frac{z}{c_i} + \frac{4}{\sqrt{\pi}} C_i \left(\frac{z}{c}\right)^2 + --\right] e^{-(z/c_i)^2} \frac{dz}{c_i dt}.$$

The numerical coefficient of the nth term is $2/\Gamma\left(\frac{n+1}{2}\right)$.

The constants c_i, A_i, B_i, C_i, $- - - -$ remain to be determined.

The integral is

$$m_i = \triangle_i \left[A_i \Pi_o\left(\frac{z}{c_i}\right) + B_i \Pi_1\left(\frac{z}{c_i}\right) + C_i \Pi_2\left(\frac{z}{c_i}\right) + --\right] + \overline{M}_i. \qquad (22)$$

The Π's are the Gaussian functions of higher order defined by

$$\Pi_n(z) = \frac{2}{\Gamma\left(\frac{n+1}{2}\right)} \int_o^z z^n e^{-z^2} dz.$$

[1] Byerly: "An Elementary Treatise on Fourier's Series, etc.," p. 83.

Those of even order are odd functions, of odd order even. At $\pm\infty$ the odd function become ± 1, the even $+1$.

The values of the constants, $C_i, A_i, B_i, ---$, will be gotten by writing the m's as solutions of equations (18). For the left hand member we have by (22)

$$q_i = -\int_{-\infty}^{x} \frac{dm_i}{dt}\,dx = -\triangle_i \int_{-\infty}^{x} \left[\frac{2}{\sqrt{\pi}} A_i + 2B_i \frac{z}{c_i} + \frac{4}{\sqrt{\pi}} C_i \left(\frac{z}{c_i}\right)^2 + -- \right] e^{-(z/c_i)^2} \frac{dz}{c_i dt}\,dx .$$

From the definition of z

$$\frac{dz}{dt}\,dx = -\frac{z}{\sqrt{t}}\,dz .$$

The integral is then

$$\frac{\triangle_i c_i}{\sqrt{t}} \int_{-\infty}^{x} \left[\frac{2}{\sqrt{\pi}} A_i \frac{z}{c_i} + 2B_i \left(\frac{z}{c_i}\right)^2 + -- \right] e^{-(z/c_i)^2} \frac{dz}{c_i} .$$

We break the integral into two terms

$$\int_{-\infty}^{x} = \int_{-\infty}^{0} + \int_{0}^{x} ,$$

and obtain

$$q_i = \triangle_i \frac{c_i}{\sqrt{t}} \left[\frac{A_i}{\sqrt{\pi}} \left(\Pi_1 \left(\frac{z}{c_i}\right) - 1 \right) + \frac{\sqrt{\pi} B_i}{2} \left(\Pi_2 \left(\frac{z}{c_i}\right) + 1 \right) + -- \right] . \quad (23)$$

The right hand member of (18) is from (20)

$$q_i = -\frac{u_i}{v_i} \frac{dm_i}{dx}$$

$$\pm u_i m_i \frac{\frac{u_1 dm_1}{v_1} + \frac{u_3 dm_3}{v_3} + ---- - \frac{u_2 dm_2}{v_2} - \frac{u_4 dm_4}{v_4} ---}{(u_1 m_1 + u_2 m_2 + --- \quad)\,dx} .$$

Writing the m's in terms of (22),

$$q_i = -\frac{u_i}{v_i} \triangle_i \left(\frac{1}{\sqrt{\pi}} A_i + B_i \left(\frac{z}{c_i}\right) + --- \right) e^{-(z/c_i)^2} \frac{1}{c_i \sqrt{t}}$$

$$\pm u_i \left[\triangle_i \left(A_i \Pi_o \left(\frac{z}{c_i}\right) + -- \right) + \overline{M}_i \right] \times$$

$$\frac{\frac{u_1 \triangle_1}{v_1} \left[\frac{A_1}{\sqrt{\pi}} + B_1 \left(\frac{z}{c_1}\right) + -- \right] e^{-(z/c_1)^2} \frac{1}{c_1 \sqrt{t}} \pm ---}{u_1 \left[\triangle_1 \left(A_1 \Pi_o \left(\frac{z}{c_1}\right) + --- \right) + \overline{M}_1 \right] + ---} . \quad (24)$$

Comparing the two expressions for q_i, (23) and (24), we see that the factor $\sqrt{t}$ cancels and any set of coefficients (A_1, B_1, $--$ A_2, B_2, $---$) which is a solution at one time will yield a solution at all times.

To secure the first n coefficients (23) and (24) may be expanded in power series in z and the coefficients of like powers equated. In order for the end concentrations to be given correctly the coefficients must satisfy the additional equations

$$A_i + B_i + C_i + --- = 1 \qquad (25)$$

$$A_i - B_i + C_i - --- = 1$$

The c_i's are also unknowns to be determined. In a system of i ionic species there will then be i (n + 2) equations to be satisfied by i (n + 1) variables. By deriving a separate solution for each side of the origin only one of (25) need be satisfied at a time, and the number of equations equals the number of variables. As the number of terms is increased the two solutions approach each other. Equation (22) then gives the distribution of the ionic species thruout the junction for the assumed force laws and boundaries.

Since the m's will be given as functions of a single variable, z, we may eliminate z and write the m's as functions of a single m independent of x or t. As the time could enter the expression for cell EMF only thru the m's, it follows that *the EMF of the cell is independent of the time.* This is due to the fact that an initial distribution has been chosen which may be written as a function of z. Indeed the above method can be applied only in such a case. If we had chosen an initial distribution which required x as an independent variable we should not have been able to eliminate either x or t from m. The EMF of such a cell would vary with time approaching as a limit the EMF of the solved case. It is then seen that *the correct way to set up a cell with transference is to form a junction with initially a sharp boundary between the electrolytes and thereafter to let them interdiffuse undisturbed.*

The rule is varied by the experiments of Cummings and Gilchrist[1] with large junctions. The unsteady p. d. observed by them when the junction was made thru a narrow capillary was presumably due to the equipotential surfaces being no longer planes, as is postulated in the present development.

First Order Solution in Detail

The expansion of (22) as far as first order terms will now be developed. In this case the m's are given as odd functions plus constant terms. The B's, C's, etc. become zero, the A's are unity; and since both of (25) are thereby satisfied the same solution applies to both sides of the origin. Values of c_i will be obtained by equating (23) and (24). Neglecting all powers of z and with $\sqrt{\pi t}$ cancelled, they appear thus

$$-\triangle_i c_i = -\frac{u_i}{v_i}\frac{\triangle_i}{c_i} \pm u_i \overline{M}_i \frac{\frac{u_1}{v_1}\frac{\triangle_1}{c_1} - \frac{u_2}{v_2}\frac{\triangle_2}{c_2} \pm ---}{S}$$

[1] Cummings and Gilchrist: "Trans. Faraday Soc., 9, 174 (1913).

where $S = u_1\bar{M}_1 + u_2\bar{M}_2 + ---$. The upper sign with i is for i a cation, lower i an anion. Transposing,

$$\mp \frac{S\,\triangle_i}{\bar{M}_i}\left(\frac{c_i}{u_i} - \frac{1}{v_i c_i}\right) = \frac{u_1\,\triangle_1}{v_1\ c_1} - \frac{u_2\,\triangle_2}{v_2\ c_2} \pm ----$$

$$- \frac{S\,\triangle_1}{\bar{M}_1}\left(\frac{c_1}{u_1} - \frac{1}{v_1 c_1}\right) = \frac{u_1\,\triangle_1}{v_2\,c_2} - \frac{u_2\,\triangle_2}{v_2\,c_2} \pm ---$$

(26)

Substracting,

$$\frac{\triangle_1}{\bar{M}_1}\left(\frac{c_1}{u_1} - \frac{1}{v_1 c_1}\right) = \pm \frac{\triangle_1}{\bar{M}_i}\left(\frac{c_i}{u_i}\ \frac{1}{v_i c_i}\right). \tag{27}$$

Similarly

$$\frac{\triangle_2}{\bar{M}_2}\left(\frac{c_2}{u_2} - \frac{1}{v_2 c_2}\right) = \mp \frac{\triangle_i}{\bar{M}_i}\left(\frac{c_i}{u_i} - \frac{1}{v_i c_i}\right).$$

Put

$$p_i \equiv \frac{c_i}{u_i} - \frac{1}{v_i c_i}.$$

Then from (27)

$$\frac{2u_1}{v_1 c_1} = \mp u_1 p_i \frac{\bar{M}_1 \triangle_i}{\bar{M}_i \triangle_1} + \sqrt{u_1^2 p_i^2 \frac{\bar{M}_1^2 \triangle_i^2}{\bar{M}_i^2 \triangle_1^2} + \frac{4u_1}{v_1}}.$$

$\frac{2\,u_2}{v_2 c_2}$ is a similar expression with the sign of p_i reversed.

Substituting these in (21)

$$\mp \frac{2p_i \triangle_i S}{\bar{M}_i} = \mp u_1 p_i \triangle_i \frac{\bar{M}_1}{\bar{M}_i} + \delta_1 \sqrt{u_1^2 p_i^2 \triangle_i^2 \frac{\bar{M}_1^2}{\bar{M}_i^2} + \frac{4u_1 \triangle_1^2}{v_1}}.$$

$$\mp u_2\ p_i\ \triangle_i \frac{\bar{M}_2}{\bar{M}_i} - \delta_2 \sqrt{u_2^2 p_i^2 \triangle_i^2 \frac{\bar{M}_2^2}{\bar{M}_i^2} + \frac{4u_2 \triangle_2^2}{v_2}} \mp ---$$

where δ_i is ± 1 as $\triangle_i$ is positive or negative. This may be simplified into

$$\mp p_i \triangle_i S = \delta_1 \sqrt{u_1^2 \bar{M}_1^2 \triangle_i^2 p_i^2 + 4u_1 \triangle_1^2 \bar{M}_i^2 / v_1}$$

$$- \delta_2 \sqrt{u_2^2 \bar{M}_2^2 \triangle_i^2 p_i^2 + 4u_2 \triangle_2^2 \bar{M}_i^2 / v_2} \pm ---$$

(28)

The equation is now in shape for numerical solution for p_i, from which c_i may be obtained. The radicals are numerically positive.

In a system of two ionic species of the same valence (28) yields

$$\frac{1}{c_1^2} = \frac{1}{c_2^2} = \frac{v}{2}\left(\frac{1}{u_1} + \frac{1}{u_2}\right)$$

in agreement with more elementary methods.

Extension to Mobilities and Activity Coefficients variable

It will now be shown how the given solution of the dynamical equations (18) may be extended to cover a more general force law that that which has been first assumed. The form of the simple law may be maintained in the general law by writing

$$F_i = \frac{I}{v_i} \log \gamma_i m_i$$

where γ_i, the activity coefficient, is a variable function of the concentrations Since the F's are subject to an arbitrary function the γ's are also subject to one.

If the γ's for all ions may be chosen so as to vary in a common ratio from one solution to another and the λ's also vary in another common ratio, we may write

$$\gamma_i = \eta K_i \lambda_i \qquad (29)$$

where K_i is a constant of the species and η is an unspecified function of the solution common to all ions. (29) would hold in certain other cases also. In binary electrolytes no test of (29) can be made unless η is restricted to unity. In that case it leads to a relation between molecular free energies and λ/λ_o ratios formally different from that commonly stated,[1] but which fits the experimental data equally well and has as much theoretical justification. No data are available on ionic conductivities in mixed electrolytes but the measurements by Bray and Hunt[2] of total conductivities indicate a similar behavior there. (29) is probably good to the same extent that the conductance-viscosity ratio is a measure of the van't Hoff coefficient.

(29) may be put in the form

$$\frac{{}_2\gamma_i}{{}_1\gamma_i} = \frac{{}_2\eta\ {}_2\lambda_i}{{}_1\eta\ {}_1\lambda_i} \qquad (29a)$$

the left hand subscripts referring to two different solutions. As only the ratio ${}_2\eta/{}_1\eta$ is needed, ${}_1\eta$ may be taken as unity. (29) and (29a) though stated in ionic terms, really involve only molecular free energies.

With this force law we have

$$dF_i = \frac{d(\eta \lambda_i m_i)}{v_i \eta \lambda_i m_i}.$$

Since

$$u_i = \frac{\lambda_i}{\alpha_i}$$

and we are assuming

$$\alpha_1 = \alpha_2 = \text{---} = \alpha,$$

$$u_i m_i = \frac{\lambda_i m_i}{\alpha}$$

$$u_i m_i\, dF_i = \frac{d(\eta \lambda_i m_i)}{v_i \alpha}.$$

[1] Taylor: "A Treatise on Physical Chemistry" **2**, 757.

[2] Bray and Hunt: J. Am. Chem. Soc., **33**, 781 (1911).

We now remove the restriction that u_i be constant and as a second approximation write

$$\eta\lambda_i m_i = \frac{\gamma_i m_i}{K_i} = a_i m_i + b_i \qquad (30)$$

$$d(\eta\lambda_i m_i) = a_i dm_i .$$

a_i and b_i are constants and are determined from the presumably known values of the m's, γ's and λ's in the two half cells, the two values of η being chosen so as to make equations (29) be satisfied as nearly as possible. From (30) now follows

$$u_i m_i = \frac{1}{\alpha\eta}(a_i m_i + b_i)$$

$$u_i m_i dF_i = \frac{a_i dm_i}{v_i \alpha\eta}.$$

By (15) we now have

$$Q = -\frac{\frac{a_1}{v_1} dm_1 - \frac{a_2}{v_2} dm_2 \pm ----}{[(a_1 m_1 + b_1) + (a_2 m_2 + b_2) + ---]\, dx}$$

and the equation of continuity (8) becomes

$$-\frac{dm_i}{\alpha\eta dt} = \frac{d}{\alpha\eta dx}\left[\frac{adm}{v_i \alpha\eta dx} \pm (a_i m_i + b_i)\frac{\frac{\alpha_1}{v_1} dm_1 \pm ---}{[(\alpha_1 m_1 + b_1) + ---]\,\alpha\eta dx}\right]. \qquad (31)$$

Comparing this with (20) we see that it is the same equation with $\alpha\eta dt$ replacing dt, αdx replacing dx, $m_i + \frac{b_i}{a_i}$ replacing m_i, and a_i replacing u_i. The solution of (20) for m_i, namely (22), is then a solution of (31) for $m_i + \frac{b_i}{a}$ $\overline{M}_i + \frac{b_i}{a_i}$ replacing $\overline{M}_i$, and z being now defined as $\frac{x}{2}\sqrt{\frac{\alpha\eta}{t}}$. Since z is the independent variable it is not necessary here to know anything about α or η. If b_i/a_i be subtracted from each side of the equation we regain the solution for m_i itself, exactly as given by (22) a_i replacing u_i. *Equation (22) is then a quite general solution, since it provides for the continuous variation of conductances and activities between practically their exact values in the two limits.*

In the case of a species present thruout the cell it is convenient to consider it as composed of two species one from each half-cell. This is a device which must be used with caution, but is here permissible. We now have for every species $\triangle_i/\overline{M}_i = \pm 1$. The variation of activity and conductivity as given in (29) and (30) is seen to be preserved. The b's vanish and

$$a_i = \eta\lambda_i ,$$

η and λ_i being the values of η and λ_i appropriate to species i in the half-cell in which it occurrs in finite concentration.

Equations (19)-(28) are in general valid for the extended force laws (29), (30), a_i replacing u_i. If the γ's are constants, η is unity and λ_i replaces u_i.

The Junction Potential Difference

The distribution of concentrations thru the liquid junction having been determined with more or less exactness the problem remains of finding the cell EMF. It may be remarked that the two are distinct problems and the assumptions made in determining the concentrations need not now be continued. It was necessary to assume various functional relations between the variables in order to solve the set of simultaneous differential equations. But once the distribution of m's is found the integration of dE_{it} can be effected by graphical methods, even when the functional relations are not given but only series of data. However the bulk of the integration may be performed analytically by Henderson's[1] formula, which will now be extended to apply to the force law of (29).

Returning to equation (1) (and neglecting transfer of solvent) it is seen that if dF_1 be interpreted as the differential of the sum of the electrode potentials the remainder is the differential of the junction p. d., E_l. As a definition we write

$$E_l = -\int t_1 dF_1 + \int t_2 dF_2 \pm ---$$

Since $\int dF_1$ *is entirely arbitrary,* E_l *is equally arbitrary and of itself without significance.* However the integration of dE_l is tantamount to the integration of dE_{it}, for the latter is easily gotten by adding on $\int dF_1$.

The transference numbers are given rigorously by

$$t_i = \frac{\lambda_i m_i}{\lambda_1 m_1 + \lambda_2 m_2 + --}.$$

Write

$$W = \lambda_1 m_1 + \lambda_2 m_2 + ---$$
$$dY = \lambda_1 m_1 dF_1 - \lambda_2 m_2 dF_2 \pm ---.$$

Then rigorously

$$dE_l = -dY/W. \tag{32}$$

On the basis of (29) alone

$$\lambda_i m_i dF_i = \frac{d(\eta \lambda_i m_i)}{v_i \eta}.$$

Write

$$Y_H = \frac{\eta \lambda_1 m_1}{v_1} - \frac{\eta \lambda_2 m_2}{v_2} \pm ---$$
$$W_H = \eta(\lambda_1 m_1 + \lambda_2 m_2 + ---).$$

Then the value of dE_l resulting from (29) is

$$dE_{lH} = \frac{-dY_H}{W_H}. \tag{33}$$

The approximation is now introduced that (k being a constant)

$$dY_H = k\, dW_H. \tag{34}$$

[1] Henderson: Z. physik. Chem., **59**, 118 (1907); **63**, 325 (1908). Planck's formula (Wied, Ann., **39**, 161 (1890); **40**, 561 (1890)) does not apply to the junction here considered. It applies to a junction in which the distribution of concentrations is maintained steady by artificial means.

The integral of (33) for a temperature of T°K is then

$$E_{1H} = -\frac{RT}{F}\frac{{}_2Y_H - {}_1Y_H}{{}_2W_H - {}_1W_H}\ln\frac{{}_2W_H}{{}_1W^H}\,. \qquad (35)$$

The subscripts $_1$ and $_2$ refer to the values of W and Y in the left and right hand half-cells respectively.

(35) will be put into more familiar form.

Write

$$\begin{aligned} U &= \lambda_1 m_1 + \lambda_3 m_3 + --\\ V &= \lambda_2 m_2 + \lambda_4 m_4 + --\\ U' &= \lambda_1 v_1 m_1 + \lambda_3 v_3 m_3 + ---\\ V' &= \lambda_2 v_2 m_2 + \lambda_4 v_4 m_4 + --- \end{aligned}$$

where the m's now denote *molalities* as commonly defined. (35) is now

$$E_{1H} = -\frac{RT}{F}\frac{{}_2\eta({}_2U - {}_2V) - {}_1\eta({}_1U - {}_1V)}{{}_2\eta({}_2U' + {}_2V') - {}_1\eta({}_1U' + {}_1V')}\ln\frac{{}_2\eta({}_2U' + {}_2V')}{{}_1\eta({}_1U' + {}_1V')}\,. \qquad (36)$$

$_1\eta$ and $_2\eta$ are the values of η which best satisfy equations (29) in the two half-cells. The λ's are the actual specific conductivities in the two half-cells and may be different in $_1U$ from what they are in $_2U$.

Equation (36) is an extension of Henderson's formula and differs from it by the presence of the factors $_2\eta$, $_1\eta$. It permits the specific conductivities to vary continuously between their exact limiting values in the two half-cells and employs activity coefficients which are also variable and quite approximately correct in many cases. By Henderson the formula was derived for infinite dilution, i. e., for constant λ and γ.

Lewis and Sargent[1] showed experimentally that for finite dilution it naturally gave better results if (constant) values of λ were used appropriate to the true concentration rather than λ_o.

The present derivation differs also from Henderson's in the avoidance of some of the crudity in the concentration distribution known as his "uniform mixing assumption." This assumption is replaced by (34), which is the correct first approximation whatever the true distribution may be.

If η be constant (34) reduces to

$$\frac{dm_1}{\triangle m_1} = \frac{dm_2}{\triangle m_2} = -----, \qquad (37)$$

from which the simple Henderson formula may be obtained. It may be shown that (37) can not be strictly true unless

$$\lambda_1 = \lambda_2 = ----,$$

and its departure from the truth is the greater the greater the differences between the λ's of the various ions. In this regard (34) and (36) are also in error and to a similar extent, as is, of course, Henderson's original formula.

Equation (36) is then in error in two respects: it is based on an energy relation (29) which is not exact, and the distribution of concentrations thru-

[1] Lewis and Sargent: J. Am. Chem. Soc., **31**, 363 (1909).

out the junction as given by (34), or (37), is not correct. In terms of E_{lH} the exact value of E_l is

$$E_l = E_{lH} + \int \left(\frac{1}{W_H} - \frac{1}{W} \right) dY. \tag{38}$$

W and W_H are values of W and W_H corresponding to equal values of Y and Y_H.

Harned has shown how to get the part of the second term which corrects for the variations of the γ's (the λ's being considered constant). His method may be modified to give the correction for the variations of the γ's from the values given by (29).

Application to a Specific Concentration Cell

We shall now give a specific example of the application of the theory which has been developed. Consider the cell at 25° C

$$Cl \mid HCl\ .1M \mid KCh\ .1M \mid Ch\ .$$

Ch stands for chlorine from the right hand half cell.

It might be thought that the concentration of chlorine would remain constant thruout the cell and that (34) might hold strictly. It may be shown however that such a distribution would introduce a set of constraints which would not balance, and the true distribution must be found by (22). This will now be done and the results then used to find the correction term of (38).

Since the correction term to the cell EMF due to the departures of the concentrations from those given by (34) is a small one due to large differences in the u's, approximate (constant) values of the u's will suffice. η is taken unity. Since only ratios are needed, we may write as u's the ratios of the λ's to one another. Only ratios of concentrations are needed, so for convenience they will be increased twenty fold. The data are then:

	Left		Right	
	H	Cl	K	Ch
u	4.84	1	1	1
$\triangle$	−1	−1	1	1
$\overline{M}$	1	1	1	1

The first step is to solve (28) for pK, i. e., p for K ion.

$$-7.84p_K = -\sqrt{4.84^2p_K^2 + 4 \times 4.84} + \sqrt{p_K^2 + 4} + \sqrt{p_K^2 + 4} - \sqrt{p_K^2 + 4}$$

$$p_K = .341$$

The c's are found from (37). For convenience we use for the 1/c's the ratios of the reciprocals.

	H	Cl	K	Ch
c	1.525	1.185	1.185	.844
1/c	.7772	1.000	1.000	1.404

(22) appears as

$$m_i = \triangle_i \Pi_o \left(\frac{z}{c_i} \right) + 1.$$

In Table I are given the solutions for a series of points thruout the junctions. The values of Π_0 are taken from the tables of Jahnke and Emde. The 6th column gives the total concentration of cation, m_+, the 7th of anion, m_-. The 8th gives the excess of cation concentration above 2, the 9th that of anion above 2. The 10th is the difference of anion and cation concentrations.

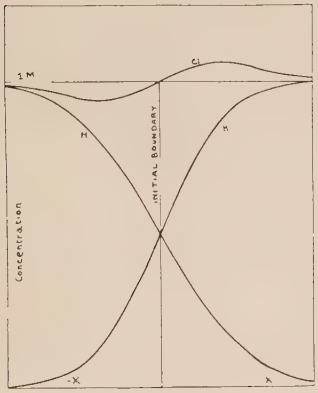

FIG. 1
Concentration Distribution at .1 M HCl KCl Junction

The values e_+, e_-, measure the departures of the true concentration distribution from that which would be given by (34) or (37). The values of $m_- - m_+$ give the error caused by the retention of but two terms in the expansion of (22). Since m_+ must equal m_- the true values probably lie between m_+ and m_- as found. The values of e_+ then give a lower limit to the departures. We accordingly accept the m_+ values in favor of the m_- as the concentration of total chlorine.

The computation is continued in Table II. Columns 2 and 3 give the values of Y and W. Here

$$Y = \lambda_1 m_1 - \lambda_2 m_2 \pm ----,$$

the m's of the preceding table being employed. In column 4 is given the value of W_H corresponding to a value of Y_H equal to Y given in 2, equation

TABLE I

1	2	3	4	5	6	7	8	9	10
z	x20 m_K	m_{Ch}	m_H	m_{Cl}	m_+	m_-	e_+	e_-	$\frac{m_- - m_+}{m_+}$
$-\infty$	.0000	.0000	2.0000	2.0000	2.0000	2.0000			
−2.0	.0047	.0001	1.9720	1.9953	1.9767	1.9954			
−1.0	.1573	.0471	1.7283	1.8427	1.8856	1.8898			
− .6	.3961	.2335	1.4904	1.6039	1.8865	1.8374			
− .2	.7773	.6913	1.1739	1.2227	1.9512	1.9140			
.0	1.0000	1.0000	1.0000	1.0000	2.0000	2.0000	.00	.00	.00
.2	1.2227	1.3087	.8261	.7773	2.0488	2.0860	.05	.09	.04
.6	1.6039	1.7665	.5096	.3961	2.1135	2.1626	.11	.16	.05
1.0	1.8427	1.9529	.2717	.1573	2.1142	2.1102	.11	.11	.00
2.0	1.9953	1.9999	.0280	.0047	2.0233	2.0046	.02	.00	−.02
∞	2.0000	2.0000	.0000	.0000	2.0000	2.0000	.00	.00	.00

(37) being employed. In column 5 is given $D = 1/W_H - 1/W$; in column 6 the sums of D's corresponding to equal positive and negative values of z, that is, to Y's which differ by equal amounts from the mean value 3.8400.

The values in column 6 plotted as ordinate against Y as abscissa then give the correction integral

$$\int_{7.68}^{0}\left(\frac{1}{W_H}-\frac{1}{W}\right)dY.$$

This is found to be $-.0130$, twice as many points being used as are shown in the tables. For 25°C this must be multiplied by .0257, (RT/F), giving the correction term $-.33$ mv. The error in Henderson's formula due to the use

TABLE II

1	2	3	4	5	6
z	Y	W	W_H	$D=1/W_H-1/W$	$D_z - D_{-z}$
$-\infty$	7.6800	11.6800	11.6800	.00000	
−2.0	7.5724	11.5258	11.5724	−.00035	
−1.0	6.6367	10.4079	10.6367	−.00207	
− .6	5.7231	9.4961	9.7231	−.00246	
− .2	4.5077	8.4101	8.5077	−.00137	
.0	3.8400	7.8400	7.8400	.00000	.00000
.2	3.1723	7.2699	7.1732	.00186	.00049
.6	1.9567	6.1839	5.9567	.00616	.00370
1.0	1.0433	5.2721	5.0433	.00862	.00655
2.0	.1076	4.1542	4.1076	.00273	.00238
∞	.0000	4.0000	4.0000	.00000	.00000

of (34) is thus seen to be very slight. However, it is an error which does not decrease with dilution, if the relative concentrations be maintained. Increasing the relative H concentration in one half-cell will produce a large correction term. The correction may amount to as much as 10 mv. but such cells would not be of practical importance. It might also be found larger if the free energy function were different from the one here used.

The principal part of the cell EMF will now be obtained by computation of E_{1H} as given by (36). The following data are available: [1, 2, 3, 4].

	Left		Right	
γ_{HCl}	.814		.803	
γ_{KCl}			.794	
λ_H	324.4	λ_{Cl} 66.0	λ_K 63.9	λ_{Cl} 65.1

The remaining data necessary to determine $_2\eta/_1\eta$ are inferred as follows: λ_K/λ_{Cl} is taken constant thruout the cell. $d\gamma_{HCl}/d\lambda_{HCl}$ is taken to have the same value from pure .1M HCl to pure .1M KCl that it has in varying

[1] Conductivities, Noyes and Falk: J. Am. Chem. Soc., **34**, 454 (1912).
[2] Activity coefficients, Lewis and Randall: "Thermodynamics," p. 362.
[3] Activity coefficient of .0M HCl in .1M KCl, Harned: J. Am. Chem. Soc., **48**, 326 (1926).
[4] n_c in HCl, Noyes: "Conductivity of Aqueous Solutions," p. 327.

concentrations of pure HCl. Comparison of data from the sources mentioned yields for pure HCl the quite constant value

$$\frac{d\gamma_{HCl}}{d\lambda_{HCl}} = 193.$$

From this λ_{HCl} in pure KCl is found to be 388.3. Similarly is found in pure KCl

$$\frac{d\gamma_{KCl}}{d\lambda_{KCl}} = 105,$$

from which γ_{KCl} in pure HCl is found to be .811. We take

$$\gamma_K = \gamma_{Cl}$$

and the complete data now appear:

	Left			Right		
	H	K	Cl	H	K	Cl
γ	.904	.901	.901	.902	.891	.891
λ	324.4	64.8	66.0	323.2	63.9	65.1

The ratio ${}_2\eta/{}_1\eta$ may now be computed from (29a). From the H data it is 1.0015 and from the K and Cl 1.0026. We adopt 1.002 for η_2, as η_1 may always be taken as unity.

These data in (36) now yield E_{lH} as 28.21 mv. Applying the correction term $-.33$ mv according to (38) we obtain the junction p. d., E_l, as 27.88 mv. The sum of the electrode p. d.'s is given by

$$-.05915 \log \frac{.901}{.891} = -.29 \text{ mv.}$$

Hence the cell EMF is 27.6 mv. The observed value according to Lewis, Brighton and Sebastian[1] is 27.8 mv. This is very satisfactory agreement, but it must be remembered that part of the data rests on conjecture. Any reasonable values for these uncertain data lead to nearly the same result however. MacInnes and Yu[2] also measured this cell using a flowing junction, and found its EMF 26.78 mv. The reason for the disparity is unknown, though the present theory does not necessarily apply in every particular to such a junction.

The simple Henderson formula assuming constant λ's and γ's reduces in this case to

$$.05915 \log \frac{\lambda_{HCl}}{\lambda_{KCl}}$$

and yields a cell EMF of 28.45 mv. The values are compared below.

E M F of Cell, Cl | .1M HCl | .1M KCl | Cl

Computed		Observed	
Henderson	Taylor	L,B&S	M&Y
28.4 mv.	27.6	27.8	26.78

[1] Lewis, Brighton and Sebastian: J. Am. Chem. Soc., **39**, 2245 (1917).
[2] MacInnes and Yu: J. Am. Chem. Soc., **43**, 2563 (1921).

The correction term for transfer of solvent (equation 6) has been estimated and found negligible.

pH Numbers from Cells with Transference

In the preceding pages we have considered the problem of computing the EMF of the cell with transference from given data. We should rather consider: Given the EMF of the general cell with transference, what information can be inferred? Owing to the complexity of such a cell it appears that very little can be inferred with certainty. In particular the determination of pH numbers by such a cell is not the simple thing it is sometimes assumed, for the cell EMF depends not only on the acid activity but also on the activity of every molecular species in the cell and mobility of every ion. If these are sufficiently well known to be allowed for, the acid activity is likely to be sufficiently well known not to need measurement.

The discussion ought to have made plain the futility of trying to eliminate the liquid junction p.d. either analytically or experimentally. The liquid junction must be regarded as a convenient grouping of terms in the expression for cell EMF and of itself without physical significance. Thus the KCl bridge should be examined in the light of the EMF of the whole cell, or we may use a half cell with hypothetical electrode, e. g.,

$$\mathrm{H} \mid \mathrm{KCl\ (sat.)} \mid \mathrm{HR} \mid \mathrm{H}.$$

The EMF by (1) is

$$E_{Ht} = \int t_K dE_{HK} + \int t_{Cl} dE_{HCl} + \int t_R dE_{HR}.$$

This may also be written

$$\int (t_K + t_{Cl})\, dE_{HCl} + \int t_R dE_{HR} - \int t_K dE_{KCl}.$$

If the concentration of HR is low t_K and t_{Cl} tend to the value .5 thruout the range of E's which contribute materially to the integral and t_R is small. *Thus the cell EMF approaches the difference between the change in free energy of HCl and one half the change of that of KCl.* How close is the approach can only be told by computing out E_{Ht}. In many cases it will be within a few millivolts, but the presence of other ions in the cell, as is commonly the case, will complicate matters, and cells are known in which E_{Ht} is even of opposite sign from the above described limit.

If we wish to postulate

$$F_K = F_{Cl}$$

these quantities, F_K and F_{Cl}, tend to cancel, and we have

$$E_{Ht} \doteq \int (t_K + t_{Cl} + t_R)\, dF_H + \int t_R dF_R.$$

This is less than the change in hydrogen ion free energy, $\triangle F_H$, by

$$\int t_H dF_H - \int t_R dF_R.$$

dF_H is approximately equal to dF_R but t_H is four or five times t_R. If a sufficient number of cells of known composition were studied it would be possible to form an idea of what the correction to a given observed E_{Ht} would be to reduce it to $\triangle F_H$.

The determination of pH numbers directly from cell EMF's in those cases where they are known to give satisfactory results is of course not to be questioned, but their uncritical use in all cases regardless of the constitution of the electrolyte can only be deplored.

The applicability of the various formulae which have been considered may now be summarized. There are two main types of junction available:

(1) a series of junctions, the gradations in concentration being made to conform to Eq. (37) or to (34). A poor approach to this is to stir the electrolytes together. The cell EMF may then be computed in ascending order of accuracy by the simple Henderson formula, the author's formula, Harned's method, a graphical correction for residual errors. No correction for concentration distribution is needed.

(12) the single, sharp, plane, large junction, which must be neither stirred nor shaken. The three formulae apply less closely than to the first junction, so that the concentration distribution should be found by equation (22) and a correction term computed, as has been exemplified. Better still is a graphical integration to correct for any variations in λ's and γ's otherwise unconsidered made on the basis of the true distribution. The second junction makes more laborious computation but gives an EMF nearer the limit desired for pH number.

It is my pleasure to acknowledge indebtedness to Professor Herbert S. Harned for many fruitful discussions concerning the subject of this paper.

Summary

I. An integral has been derived for the EMF of the general cell with transference, Eq. (5), including the effect of solvent transfer, (6).

II. The differential equation of diffusion of electrolytes, (14), is derived rigorously, and is shown to depend on molecular free energies only and to be independent of ionic free energies.

III. From this it is shown that the EMF of the cell with transference is independent of ionic free energies, and that ionic free energies may always be chosen in each solution to satisfy any single arbitrary function (not a function of the molecular free energies) without thermodynamic error.

IV. A method is given for finding the distribution of concentrations thruout a junction under conditions sufficiently broad to make it generally applicable.

V. Henderson's formula for liquid junction p. d's. is extended to provide for variable mobilities and activity coefficients. The formula is an approximation and it is shown how to get the correction as a graphical integral.

VI. The theory applied to the tenth normal HCl | KCl cell gives much better results than have been obtained heretofore by the simple Henderson formula.

VII. The bearing of these results on pH determination are considered.

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